

# Effects of ultrasound on the electrodeposition of lead dioxide on glassy carbon electrodes

José González-García, Jesús Iniesta, Antonio Aldaz and Vicente Montiel\*

Grupo de Electroquímica Aplicada, Departamento de Química Física, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain

The electrodeposition of lead dioxide from lead(II) nitrate in an acid medium has been used as a test reaction to study the effects of an ultrasound field. The different behaviours found between platinum and glassy carbon electrodes have been compared by means of cyclic voltammetry and simple potential steps. The current–time response for a platinum electrode is not affected by the presence or absence of ultrasound; in contrast, significant changes have been observed in the characteristic regions of these curves (induction time  $t_0$ ) with the glassy carbon electrode. Scanning electron microscopy (SEM) has been employed to follow changes in the surface topography after the electrodes had been exposed to ultrasound. Results indicate that neither pits nor structural modifications that may increase the electrode surface occur with the device used. It is concluded that the activation of glassy carbon electrodes by the action of an ultrasound field for electrodeposition of lead dioxide is associated with the surface functionalization caused by the reaction of OH<sup>•</sup> radicals (derived from aqueous sonolysis) with the carbon surface.

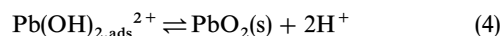
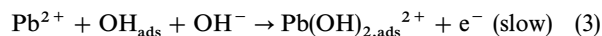
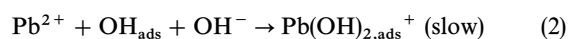
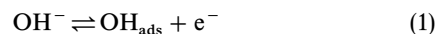
Nowadays, the influence of ultrasound on the electrochemical behaviour of different systems is a very active field of research.<sup>1</sup> Thus, beneficial effects have been found on mass transport,<sup>2,3</sup> on activation of the electrode surface,<sup>4</sup> on adsorption processes,<sup>5</sup> and on the modifications that occur in the reaction mechanisms due to radical generation<sup>6,7</sup> when electrochemical processes are carried out under ultrasonic irradiation. In most of these studies the reduction of ferricyanide anion,<sup>8</sup> methylviologen,<sup>9</sup> *p*-benzoquinone,<sup>10</sup> copper sulfate,<sup>11</sup> and the oxidation of pyrrole<sup>12</sup> have been used as test reactions in order to obtain information on the changes that occur in the different types of electrochemical processes. The influence of ultrasounds on the electrode surface of different materials have also been studied.<sup>13</sup> Coury and coworkers<sup>13</sup> have studied substrates such as glassy carbon, Ebonex, Pt, Au, W and Pd, and they have laid great stress on the effects of ultrasound on glassy carbon.

A wide diversity of methods have been reported for the treatment and activation of surfaces of carbon electrodes. There are very different and even controversial opinions about the reproducibility of the results.<sup>14,15</sup> In any case, there is agreement that the oxidation of the surface of glassy carbon provides an increase in the activity of the electrode.<sup>16–18</sup>

In this context, we can also find in the literature other studies in which pretreatment with ultrasound of the electrode surface, used in electrochemical studies, provides an activated surface.<sup>19</sup> In that particular paper,<sup>19</sup> glassy carbon electrodes that had been irradiated with ultrasound in dioxane exhibited an increase of activity in the heterogeneous electron transfer for a variety of aqueous redox probes. However, when sonication was performed in water, no significant enhancement was observed, but severe surface pitting was noticeable. In addition, an increase in the density of electroactive surface oxides was evident, which were probably produced as a result of the reaction between OH<sup>•</sup> radicals generated in the aqueous sonolysis and the surface.<sup>20,21</sup>

In this paper we propose the electrodeposition of lead dioxide from soluble salts of Pb<sup>II</sup> as a test reaction to study

the effects of ultrasound on the electrode surface. Fleischmann *et al.*<sup>22–25</sup> were the first to investigate the mechanism for the electrodeposition of lead dioxide. They suggested the following mechanism:



Several authors, like Chang and Johnson<sup>26,27</sup> and Velichenko *et al.*<sup>28</sup> have recently proposed some modifications to this mechanism. Thus, they suggest that the mechanism involves the generation of some soluble intermediates, which can be withdrawn from the electrode surface by means of convective–diffusional processes. Anyhow, it should be noted that the first step in the mechanism (generation of OH<sub>ads</sub>) has been widely accepted.<sup>29–35</sup>

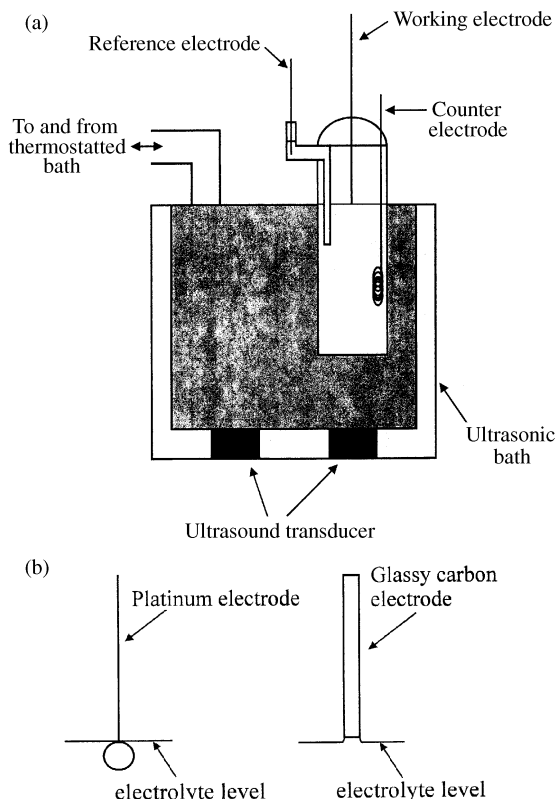
## Experimental

All experiments were carried out using a Voltalab electrochemical system consisting of a DEA 332 potentiostat and an IMT 102 electrochemical interface. The system was connected to a personal computer for recording and treatment of curves.

Electrochemical experiments were performed in a typical all-glass two-compartment voltammetric cell (50 mL volume) placed just over the transducer of a Selecta commercial ultrasonic bath (30 kHz, 100 W). The cell was immersed in such a way that the level of both liquids (bath and electrolyte) was the same. The level of the bath liquid was 6 cm from the bottom, and this was the separation distance between the transducer and the electrode surface (Fig. 1). The system was thermostatted by recirculating water at a constant temperature of 25 °C.

The working electrodes were a polyoriented platinum electrode and a glassy carbon rod. A platinum wire acted as the counter electrode. Platinum electrodes were cleaned by

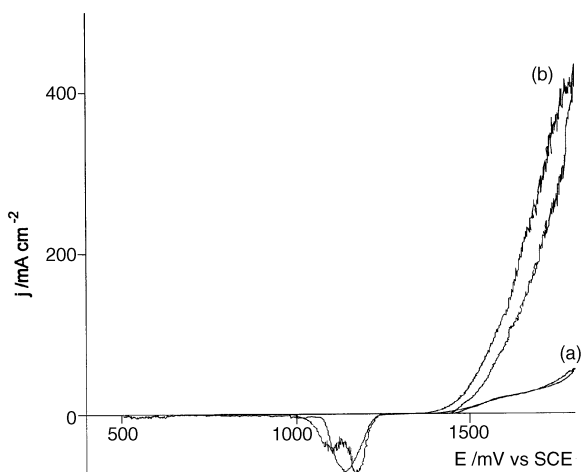
E-mail: vicente.montiel@ua.es



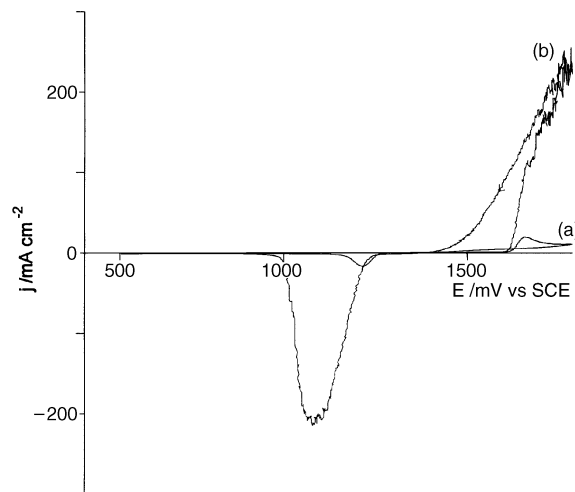
**Fig. 1** (a) Diagram of the experimental cell and the sonication arrangement. (b) Electrode location at electrolyte surface in the electrochemical cell

heating to red heat and quenching in water prior to each experiment. Before each experiment, glassy carbon electrodes were polished, first with fine emery paper, then with decreasing size alumina particles in suspension on a polishing cloth, until a mirror finish was obtained. In both cases, electrodes were thoroughly rinsed with water. A SCE served as the reference electrode.

The chemicals were Analar quality. Aqueous solutions of 0.1 M lead(II) nitrate–1 M nitric acid were prepared using ultrapure water obtained from a Millipore Milli-Q system. Solutions were thoroughly purged of oxygen prior to sweeping by bubbling with nitrogen N50 (Air Liquide) for 20 min. Nitrogen N50 (Air Liquide) was also used for saturation



**Fig. 2** Cyclic voltammogram in 1 M HNO<sub>3</sub> + 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> at a polyoriented platinum electrode,  $v = 5 \text{ mV s}^{-1}$ . (a) Silent, (b) ultrasonic conditions



**Fig. 3** Cyclic voltammogram in 1 M HNO<sub>3</sub> + 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> at a glassy carbon electrode,  $v = 5 \text{ mV s}^{-1}$ . (a) Silent, (b) ultrasonic conditions

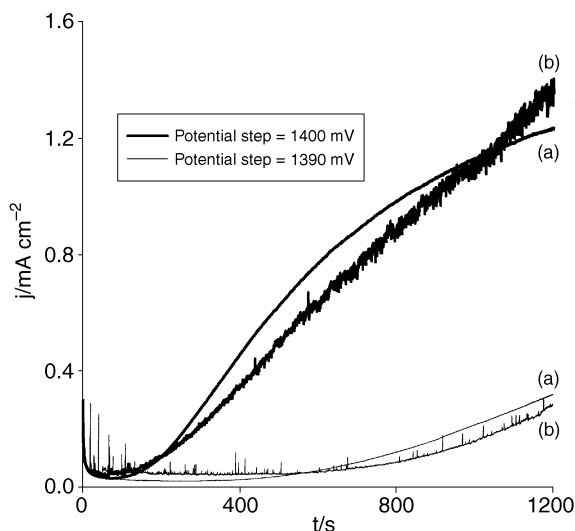
gassing of the solutions before each experiment. During measurements a flow of gas was passed over the solution surface.

A JSM-840 JEOL scanning electron microscope was employed to obtain topographical views of the electrode surfaces.

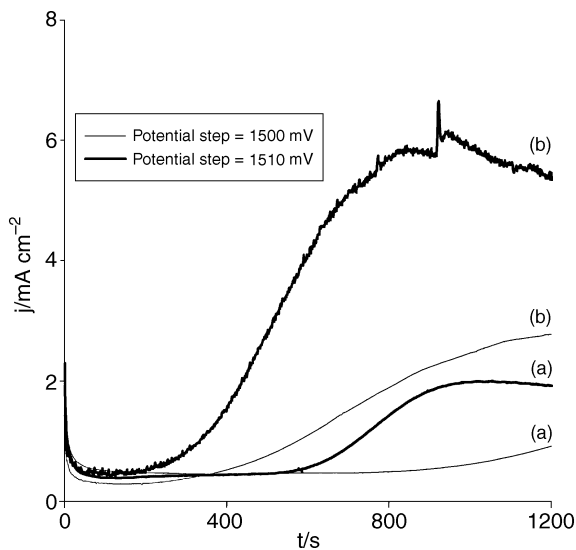
## Results

### Voltammetry

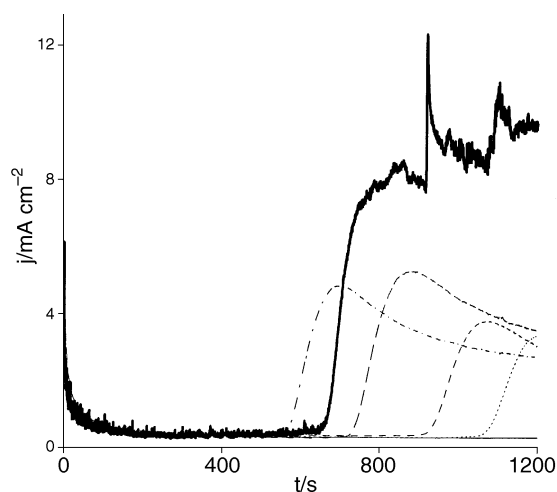
Fig. 2 shows the cyclic voltammogram of the electrodeposition of lead dioxide from 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> + 1 M HNO<sub>3</sub> on a platinum electrode recorded under silent (a) and ultrasonic (b) conditions. Fig. 3 shows the same experiment on a glassy carbon electrode. The voltammetric response for platinum is the same under both silent and ultrasonic conditions, except in the mass transport control region, as might be expected. Analogous behaviour is observed for a glassy carbon electrode. However, the potential at which electrodeposition begins is different for each electrode. It can, therefore, be deduced that the activation overpotential for platinum is significantly less than that for glassy carbon. This same behaviour, which has also been observed for the oxygen evolution process, is consistent with the conclusion drawn by many researchers,<sup>26,36,37</sup> whereby the initial step (eqn. 1) in the lead dioxide electrodeposition mechanism is the same as that for



**Fig. 4** Chronoamperometric curves for PbO<sub>2</sub> deposition in 1 M HNO<sub>3</sub> + 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> at a polyoriented platinum electrode. (a) Silent, (b) ultrasonic conditions



**Fig. 5** Chronoamperometric curves for  $\text{PbO}_2$  deposition in 1 M  $\text{HNO}_3$  + 0.1 M  $\text{Pb}(\text{NO}_3)_2$  at a glassy carbon electrode. (a) Silent, (b) ultrasonic conditions



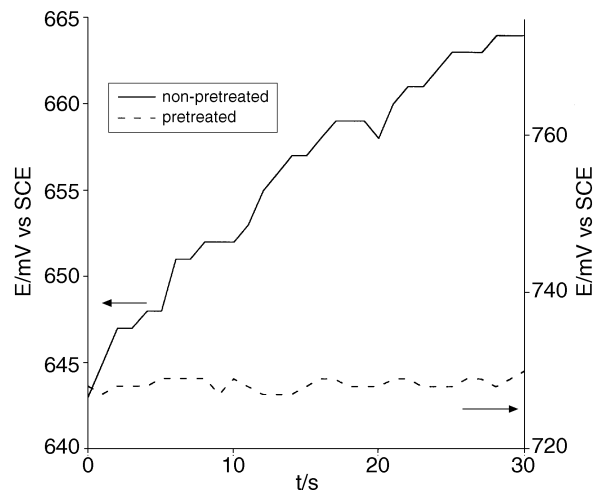
**Fig. 6** Chronoamperometric curves for  $\text{PbO}_2$  deposition in 1 M  $\text{HNO}_3$  + 0.1 M  $\text{Pb}(\text{NO}_3)_2$  at a glassy carbon electrode with different ultrasonic pre-treatment times. — Pretreatment time = 0 min. Silent. ..... Pretreatment time = 5 min. Silent. --- Pretreatment time = 10 min. Silent. -.-.- Pretreatment time = 15 min. Silent. -.-.- Pretreatment time = 20 min. Silent. — No pre-treatment. Under ultrasound

oxygen evolution on a variety of electrodes. It is noteworthy that the electric charge of the stripping process of lead dioxide on platinum ( $E \approx 1130$  mV vs. SCE) is less than the electric charge on glassy carbon. This is a consequence of the poor adherence of lead dioxide to the platinum electrode, as is demonstrated by the presence of lead dioxide flakes at the bottom of the cell during the experiment.

### Chronoamperometry

Potential step experiments were performed in two stages. In the first stage, the electrode was held in an open circuit ( $j = 0$ ) for 30 s. In a second stage, and immediately after, a potential step that has been fixed beforehand was carried out. In some experiments (Fig. 6), the electrode underwent additional pretreatment with ultrasound in which the variable was the duration of this pretreatment.

Fig. 4 shows the  $j-t$  profiles for lead dioxide deposition on a polyoriented platinum electrode under silent (a) and ultrasonic



**Fig. 7**  $E-t$  curves in 1 M  $\text{HNO}_3$  + 0.1 M  $\text{Pb}(\text{NO}_3)_2$  at glassy carbon electrodes

conditions (b) for two steps of different amplitudes. It can be seen that both transient curves are very similar but with slightly lower  $j$  values in the presence of ultrasound.

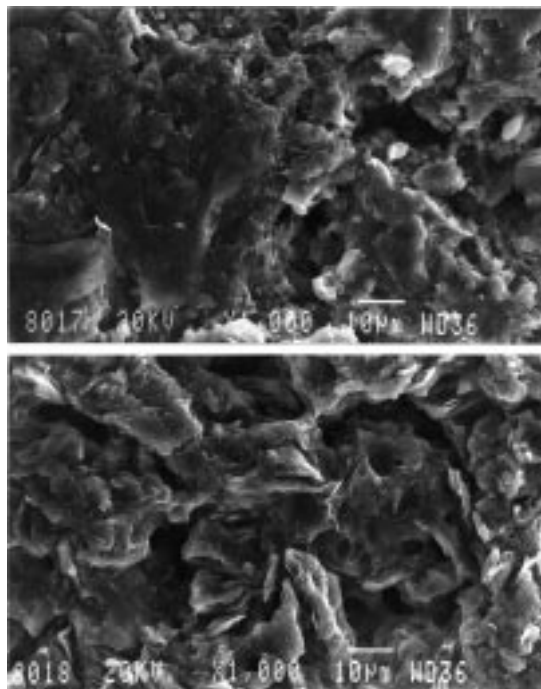
Fig. 5 shows the chronoamperometric transients for a glassy carbon electrode under silent (a) and ultrasonic conditions (b) for two steps of different amplitudes. In this case, a strong influence of the ultrasound field can be pointed out. Thus, the induction time under ultrasonic conditions is less than under silent conditions and the current density is higher under ultrasound than under silent conditions. Coury and coworkers<sup>13</sup> have shown that glassy carbon and Ebonex electrodes are severely pitted under ultrasound in aqueous media. This is one of the reasons they argue against the use of glassy carbon for sonoelectrochemical studies in aqueous media. Scanning electron microscopy (SEM) has been employed to follow changes in the surface topography before and after the electrodes had been exposed to ultrasound in electrolytic medium for 20 min. No damage of the surface was observed. A very plausible explanation of this different behaviour is the experimental approach used in both experiments. Thus, Coury and coworkers used a sonoelectrochemical reactor that allows a sonic horn to be located a very short distance away from the electrode surface. In our work, we immersed the electrochemical cell in the ultrasonic bath, and it is known that in this configuration the ultrasound power transmitted is much lower than in the other arrangement.<sup>38</sup>

Fig. 6 shows the superposition of  $j-t$  profiles recorded in a quiescent solution on a glassy carbon electrode (pretreated *in situ* with ultrasound for different times) and in solution under ultrasound. On increasing the pretreatment times, the  $j-t$  curve recorded under quiescent conditions becomes similar to the response recorded under ultrasound.

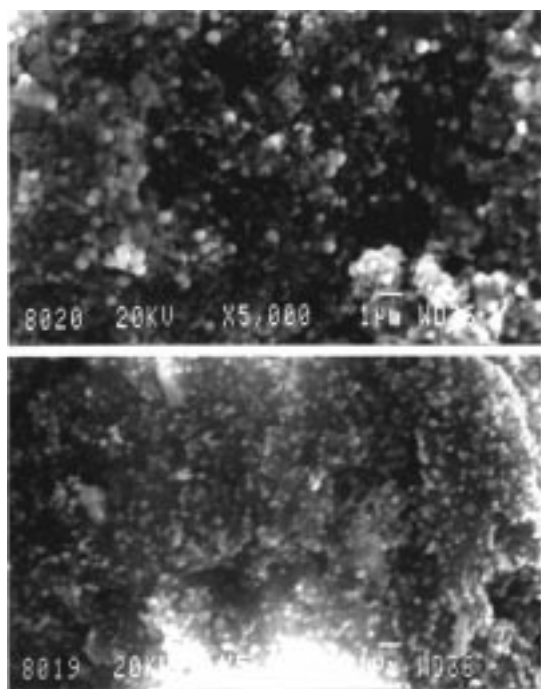
Fig. 7 shows the superposition of potential-time curves prior to the chronoamperometric experiment for the 20 min pretreatment curve and the curve recorded under ultrasound shown in Fig. 6. The electrode potential for surfaces pretreated with ultrasound is always held constant within a short interval.

Fig. 8 shows the scanning electron micrographs (SEMs) corresponding to a graphite surface before and after sonication (20 min) in the same electrolytic medium. No appreciable surface effect is evident.

Fig. 9 shows the SEMs of the lead dioxide electrodeposition process at the induction period (400 s) under quiescent conditions and under ultrasound. It is evident that the influence of ultrasound increases considerably the number of particles of lead dioxide deposited at the same potential.



**Fig. 8** Scanning electron micrographs of a graphite surface (above) before and (below) after sonication in the electrolytic medium for the experimental time (20 min)



**Fig. 9** Scanning electron micrographs of a graphite surface at the induction time (400 s) during a lead dioxide electrodeposition chronoamperometric experiment under (above) silent and (below) ultrasonic conditions

## Discussion

The interpretation of the cyclic voltammetry curves provides little information about the effects of an ultrasonic field on the electrodeposition process. However, other electroanalytical techniques like chronoamperometry have been useful to contribute details of the process.

Chronoamperometric experiments have shown that the results obtained for platinum and glassy carbon are different. No noticeable effect is produced on platinum electrodes. The

small decrease in the current density has also been observed by other workers<sup>26,27</sup> under convective conditions. In contrast, the response for the glassy carbon electrode shows a more complex reaction. This makes the existence of effects located on the electrode surface evident. SEMs confirm that the surface of the sonicated electrode does not exhibit any signs of superficial pitting or damage. Therefore, no modifications of the geometric area must be expected for electrochemical measurements.

On the other hand, some new signs have been found regarding the formation of functional groups on the surface of the electrode during sonication. These functional groups persist with time. This phenomenon had previously been observed by Coury and coworkers using other test reactions and techniques.<sup>13,19</sup> When lead dioxide electrodeposition is used as a test reaction, these functional groups play a very active role in the electrodeposition mechanism (reaction 1) as an intermediate product, and they can be consumed within the process of lead dioxide deposition. This is evident in the decreasing induction time as the pretreatment time increases (or by recording the curve under ultrasound). In addition, the idea of the functionalization of the glassy carbon electrode surface as a consequence of the action of ultrasound on the surface is reinforced by the different behaviour in the  $E-t$  response for pretreated and non-pretreated electrodes. The fact that the potential remains constant with time for pretreated electrodes is evidence that treatment provides a stable surface, in contrast with non-pretreated electrodes, whose surfaces undergo changes with time, as the spontaneous variation of the potential at open-circuit indicates. The reaction of the hydroxyl radical  $\text{OH}^\cdot$ , derived from aqueous sonolysis, with the free carbon surface catalyses the nucleation process on the surface, decreasing the induction time for a constant step potential. This decrease depends on pretreatment time.

## Conclusion

The results described in this paper show that the application of an ultrasound field activates the lead dioxide electrodeposition on glassy carbon surfaces. The enhancement of this process is probably associated with an increase in the density of electroactive superficial oxides. Thus, glassy carbon is a suitable material for the kinetics studies of these processes and for other studies in which eqn. 1 occurs.

The design of the experiment used in this work can be appropriate for mechanistic studies in sonoelectrochemistry with non-metals, which are severely damaged by sonic horns located a short distance away from the electrodes.

## Acknowledgements

The authors wish to thank Dr. J. Mostany and Prof. B. R. Scharifker, Departamento de Química, Universidad Simón Bolívar, Venezuela, for their interest in this work. The authors also thank "Consellería de Cultura, Educación y Ciencia" (project GV-2231-94) and "D.G.I.C.Y.T" (project QUI97-1086) for their financial support.

## References

- (a) D. J. Walton and S. S. Phull, *Sonoelectrochemistry, Review in Advances in Sonochemistry*, ed. T. J. Mason, JAI Press, 1995, vol. 4.  
(b) R. G. Compton, J. C. Eklund and F. Marken, *Electroanalysis*, 1997, **9**, 509.
- J. P. Lorimer, B. Pollet, S. S. Phull, T. J. Mason, D. J. Walton and U. Geissler, *Electrochim. Acta*, 1996, **41**, 2737.
- R. G. Compton, J. C. Eklund, S. D. Page, T. J. Mason and D. J. Walton, *J. Appl. Electrochim.*, 1996 **26**, 775.
- R. G. Compton, J. C. Eklund, S. D. Page, G. H. W. Sanders and J. Booth, *J. Phys. Chem.*, 1994, **98**, 12410.

- 5 D. J. Walton, S. S. Phull, A. Chyla, J. P. Lorimer, T. J. Mason, L. D. Burke, M. Murphy, R. G. Compton, J. C. Eklund and S. D. Page, *J. Appl. Electrochem.*, 1995, **25**, 1083.
- 6 R. G. Compton and F. M. Matysik, *Electroanalysis*, 1996, **8**, 218.
- 7 R. G. Compton, J. C. Eklund and S. D. Page, *J. Phys. Chem.*, 1995, **99**, 4211.
- 8 C. R. S. Hagan and L. A. Coury, Jr., *Anal. Chem.*, 1994, **66**, 399.
- 9 J. Klima, C. Bernard and C. Degrand, *J. Electroanal. Chem.*, 1994, **367**, 297.
- 10 R. G. Compton, J. C. Eklund, F. Marken and D. N. Waller, *Electrochim. Acta*, 1996, **41**, 315.
- 11 J. Reisse, H. Francois, J. Vandercammen, O. Fabre, A. Kirsch-de Mesmaeker, C. Maersalk and J.-L. Delplancke, *Electrochim. Acta*, 1994, **39**, 37.
- 12 A. Benahcene, C. Petrier, G. Reverdy and P. Labbe, *New J. Chem.*, 1995, **19**, 989.
- 13 N. A. Madigan, C. R. S. Hagan, H. Zhang and L. A. Coury, Jr., *Ultrason. Sonochem.*, 1996, **3**, 239.
- 14 M. Kopanica and F. Vidra, *J. Electroanal. Chem.*, 1971, **31**, 175.
- 15 W. E. Van der Linden and J. W. Dieker, *Anal. Chim. Acta*, 1980, **119**, 1.
- 16 K. J. Stults, P. M. Kovach, W. G. Kurh and R. M. Wightman, *Anal. Chem.*, 1983, **55**, 1632.
- 17 C. E. Plock, *J. Electroanal. Chem.*, 1969, **22**, 185.
- 18 M. Noel and P. N. Anantharaman, *Analyst*, 1985, **110**, 1095.
- 19 H. Zhang and L. A. Coury, Jr., *Anal. Chem.*, 1993, **65**, 1552.
- 20 N. Serpone, R. Terzian, M. Hidaka and E. Pelizzetti, *J. Phys. Chem.*, 1994, **98**, 2634.
- 21 T. J. Mason, *Practical Sonochemistry*, Ellis Horwood, Chichester, 1991, p. 26.
- 22 M. Fleischmann and M. Liler, *Trans. Faraday Soc.*, 1958, **54**, 1370.
- 23 M. Fleischmann and H. R. Thirsk, *Electrochim. Acta*, 1959, **1**, 146.
- 24 M. Fleischmann and H. R. Thirsk, *Electrochim. Acta*, 1960, **2**, 22.
- 25 M. Fleischmann, J. R. Mansfield, H. R. Thirsk, H. G. E. Wilson and L. Wynne-Jones, *Electrochim. Acta*, 1967, **12**, 967.
- 26 H. Chang and D. C. Johnson, *J. Electrochem. Soc.*, 1989, **136**, 17.
- 27 H. Chang and D. C. Johnson, *J. Electrochem. Soc.*, 1989, **136**, 23.
- 28 A. B. Velichenko, D. V. Girenko and F. I. Danilov, *Electrochim. Acta*, 1995, **40**, 2803.
- 29 A. C. Ramamurthy and T. Kuwana, *J. Electroanal. Chem.*, 1982, **135**, 243.
- 30 H. A. Laitinen and N. H. Watkins, *J. Electrochem. Soc.*, 1976, **123**, 804.
- 31 F. Beck, *J. Electroanal. Chem.*, 1975, **65**, 231.
- 32 F. Beck and H. Boh, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 233.
- 33 N. A. Hampson, P. C. Jones and R. F. Phillips, *Can. J. Chem.*, 1968, **46**, 1325.
- 34 N. A. Hampson, P. C. Jones and R. F. Phillips, *Can. J. Chem.*, 1967, **45**, 2039.
- 35 N. A. Hampson, P. C. Jones and R. F. Phillips, *Can. J. Chem.*, 1967, **45**, 2045.
- 36 I. H. Yeo, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1987.
- 37 M. R. Tarasevich, A. Sadkowsky and E. Yager, *Comprehensive Treatise of Electrochemistry*, eds. B. E. Conway, J. O'M. Bockris, E. Yeager, S. U. M. Khan and R. E. White, Plenum Press, New York, 1983, vol. 7.
- 38 T. J. Mason and J. P. Lorimer, in *Practical Sonochemistry, User's Guide to Applications in Chemistry and Chemical Engineering*, Ellis Horwood, Chichester, 1989

*Received in Orsay, France, 17th June 1997;  
Paper 7/08754C*